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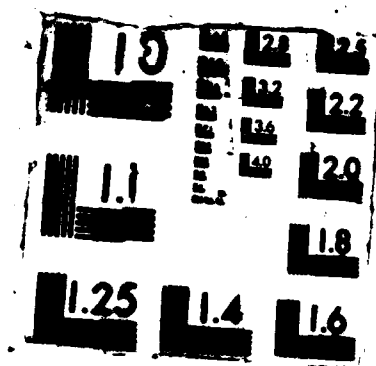
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Optical Probes of Interlamellar Redox Chemistry:
Intercalation of the Creutz-Taube Complex into Hydrogen
Uranyl Phosphate

by

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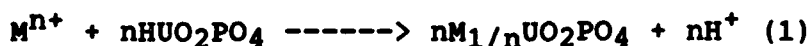
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Hydrogen uranyl phosphate (HUP) can be intercalated by the Creutz-Taube (C-T) complex, $[[Ru(NH_3)_5]_2(pyrazine)]^{2+}$, to yield hydrated, partially-substituted lamellar solids, $H(C-T)UP$, of approximate composition $H_{1-5}x(C-T)_xUO_2PO_4$ ($0.001 < x < 0.01$). The more crystalline samples exhibited an X-ray powder pattern similar to that of HUP: the structure can be indexed in tetragonal symmetry and possesses an interlamellar spacing of 68.69 Å. The absorption spectrum of $H(C-T)UP$ appears to be a simple superposition of bands due to the UO_2^{2+} moiety and the C-T complex. Photoluminescence (PL) of $H(C-T)UP$ is quenched relative to HUP; PL decay curves are nonexponential and span a shorter time domain relative to HUP. Exposure of $H(C-T)UP$ to Br_2 vapor causes the purple solid to become yellow. The spectral changes are consistent with redox chemistry wherein the intercalated C-T complex undergoes oxidation. For most samples examined, the PL decay times were enhanced upon oxidation. (Keywords:)					
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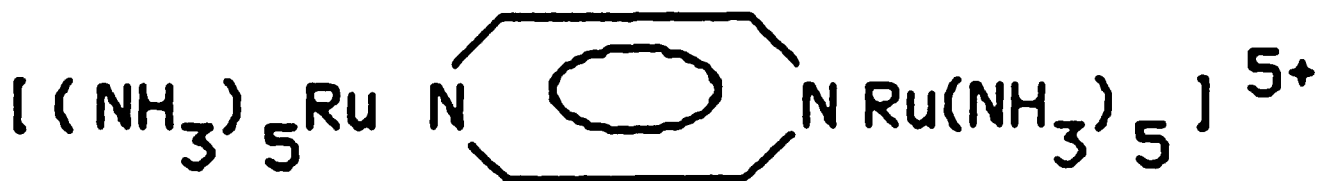
1. Introduction

In recent studies we have examined the excited-state properties of lamellar solids derived from $\text{H}_2\text{UO}_2\text{PO}_4$ (HUP) [1-5]. The parent solid yields bright green photoluminescence (PL) characteristic of the UO_2^{2+} moiety and engages in intercalative ion-exchange reactions with a variety of mono-, di-, and trivalent cations, as shown in eq. (1). We have found evidence for efficient



excited-state, host-to-guest energy transfer using $\text{Cr}(\text{NH}_3)_6^{3+}$ [2] and Eu^{3+} [4] as guest species: selective excitation of the host UO_2^{2+} chromophore leads to photoprocesses characteristic of the guest.

These experiments prompted us to consider whether larger and more highly-charged metal complexes having novel optical properties can be incorporated into the HUP lattice. The binuclear, pentavalent Creutz-Taube (C-T) complex shown below, $\{[\text{Ru}(\text{NH}_3)_5]_2(\mu\text{-pyrazine})\}^{5+}$, attracted our attention in this regard. The C-T complex is



the archetypical mixed-valence complex and exhibits a characteristic intervalence band in the near infrared portion of the spectrum [6]. Furthermore, the complex is readily reduced and oxidized.

In this paper we report that the C-T complex can be intercalated into HUP to yield a family of partially-substituted lamellar solids. Intercalation perturbs the PL properties of the host lattice. Moreover, we demonstrate that the C-T complex can be oxidized in the lattice, leading to dramatic optical effects.

2. Experimental procedure

The complexes $[\text{ClRu}(\text{NH}_3)_5]\text{Cl}_2$ [7] and $\{[\text{Ru}(\text{NH}_3)_5]_2(\mu\text{-pyrazine})\}^{4+}[\text{ZnCl}_4]_2$ [8], were prepared according to literature procedures using $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ (Johnson-Matthey), ZnCl_2 and pyrazine (Aldrich) as precursors. The mixed-valence C-T complex (pentahydrated) and its hexavalent oxidation product, $\{[\text{Ru}(\text{NH}_3)_5]_2(\mu\text{-pyrazine})\}^{6+}$, were prepared from the tetravalent species by the published procedure [8] with the exception that $\text{Na}_2\text{S}_2\text{O}_8$ (Aldrich) was used as the oxidizing agent. An absorption spectrum [6] and elemental analysis (Schwarzkopf Microanalytical Laboratory, Woodside, NY) confirmed the identity and purity of the C-T complex. Calcd. for $\text{C}_4\text{H}_{44}\text{N}_{12}\text{O}_5\text{Cl}_5\text{Ru}_2$: C, 6.7; H, 6.1; N, 23.4. Found: C, 6.7; H, 5.3; N, 22.4. Hydrogen uranyl phosphate

(HUP) was prepared as previously described [1].

Intercalation of the C-T complex into HUP was achieved by slurrying 0.5 g of HUP in 20 mL of 0.06-0.6 mM aqueous solutions of the C-T complex at room temperature for one day; complete uptake of the C-T complex corresponds to compositions of $H_{1-5x}(C-T)_xUO_2PO_4 \cdot yH_2O$ with x ranging from 0.001 to 0.01. The resulting purple solids were washed with triply-distilled water, air-dried for ~6 h, and then stored in tightly-stoppered vials. Spectrophotometric analyses of the hydrated intercalated materials were obtained by dissolving known quantities of the solids in 2 M HCl and measuring the absorbance at 565 nm; the extinction coefficient of $2.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ measured in aqueous solution was used [6], since the value was found to be unaffected by the addition of UO_2^{2+} ions (nitrate salt) and H_3PO_4 to solutions of the C-T complex that have first been acidified with 2 M HCl.

Oxidation of the intercalated solids, $H(C-T)UP$, was accomplished by placing the sample in a 2-L vessel saturated with Br_2 vapor (Fisher) for 12 h.

An X-ray diffraction powder pattern of the solid was obtained using a Philips Electronic Instruments PW 1729 X-ray source and Debye-Scherrer camera. Exposure times were 2 h to Ni-filtered Cu K α radiation. The patterns were measured to ± 0.05 mm with a Norelco film recorder and indexed in tetragonal symmetry.

Instrumentation for obtaining IR spectra (KBr pellet)

has been described [1]. Visible and near-IR electronic spectra were obtained using a Cary 17-D spectrophotometer. Although visible spectra could be acquired using a silicone grease mull on filter paper [1], KBr pellets of the solid (KBr pellet reference) were more effective for obtaining spectra in the near-IR region of the spectrum. Uncorrected 295 K PL spectra and radiative quantum yields were obtained with an Aminco-Bowman spectrophotofluorimeter, as previously described [1]. Lifetime measurements were obtained at 295 K with 450-nm excitation; their acquisition differs from a previous description [1] in the use of a fiber optic cable for light collection and a Molelectron UV-12 nitrogen laser/DL-II dye laser for excitation.

3. Results and Discussion

In sections below we discuss the synthesis and structural properties of the intercalated complex, its optical properties, and the effects of chemical oxidation on the solid.

3.1 Synthesis and structural properties

When HUP is slurried with deep purple aqueous solutions of the C-T complex, the yellow-green solid rapidly acquires the purple color of the complex. At C-T complex solution

concentrations corresponding to up to ~5% of maximum incorporation, i.e., $H_{0.95}(C-T)_{0.01}UO_2PO_4$, the filtrate is colorless, and spectrophotometric analysis indicates essentially complete uptake; beyond this concentration, the filtrate retains some of its purple color. Our study is restricted to samples with ~0.5 to 5% of maximum incorporation which corresponds to $H_{1-5x}(C-T)_xUO_2PO_4$ ($0.001 < x < 0.01$), abbreviated hereafter as $H(C-T)UP$.

Samples of $H(C-T)UP$ were characterized by X-ray diffraction powder patterns. For some of the samples, the diffraction lines were too broad to obtain accurate data, perhaps due to partial dehydration. For the more crystalline samples, the patterns could be indexed in tetragonal symmetry and indicated the presence of a single phase. Both the a -lattice value of 6.99 \AA and the interlamellar spacing of 8.69 \AA were identical to that of HUP [1], indicating that the guest species has not substantially perturbed the lattice.

An infrared spectrum of $H(C-T)UP$ exhibits a strong, sharp phosphate stretching band at 1000 cm^{-1} , confirming retention of the lamellar structure [1]. Also evident is a band at 3250 cm^{-1} , indicating that the sample is hydrated. We had hoped to see additional bands that are characteristic of the C-T complex, but they were too weak to be observed at these concentrations [6].

3.2 Optical properties

An electronic absorption spectrum of H(C-T)UP is presented in fig. 1. To a good approximation the spectrum is a superposition of the structured HUP absorption envelope and the bands arising from the C-T complex. The vibronic structure of the former lies at wavelengths below 500 nm and is characteristic of the UO_2^{2+} moiety. Bands due to the C-T complex with maxima at 565 and 1620 nm have been given charge-transfer and intervalence assignments, respectively [6]. Physical mixtures of HUP and the C-T complex yield nearly identical visible spectra to those of H(C-T)UP with the exception that the UO_2^{2+} bands are sharper; broadening of these bands has been observed in other HUP derivatives, as well [4,5]. One other noteworthy feature is that the intervalence band maximum at 1620 nm appears modestly red-shifted relative to its position in H_2O of 1560 nm [6].

Intercalation substantially reduces the intense emission characteristic of HUP. Because the UO_2^{2+} PL at 500-620 nm overlaps the intense absorption of the C-T complex, we initially thought that the reduction in PL intensity was simply due to self-absorption of the emitted light. However, physical mixtures of HUP and the C-T complex that are absorbance-matched to H(C-T)UP samples emit much more brightly with near-UV excitation, suggesting that a quenching mechanism is operating. For

example, a radiative quantum yield for a $\text{H}_{0.97}(\text{C-T})_{0.006}\text{UP}$ sample, uncorrected for self-absorption, is 0.004. While this is only a lower limit to the true value, it is nonetheless far below the 0.7 value measured for HUP [1] and well below that for an absorbance-matched physical mixture which is 0.07.

More definitive confirmation of quenching is provided by lifetime measurements: although decays are nonexponential, they typically span a temporal range of 25 to 100 μsec , compared to the 450 μsec characteristic of HUP [1]. The lack of exponential decay could arise if the C-T complex occupies a multiplicity of lattice sites characterized by different quenching efficiencies. In this scenario, the C-T complex need not even be uniformly dispersed; if efficient migration of energy occurs in the $(\text{UO}_2\text{PO}_4)_n^{n-}$ sheets, the complex could act as a killer center for a large region of the solid. With regard to a quenching mechanism, both energy and electron transfer are possible: the complex has low-lying excited states and is oxidizable.

3.3 Chemical oxidation

The ability of the C-T complex to undergo redox chemistry in solution (E^0 is +0.76 V vs. SHE [6]) caused us to examine whether it would do so once intercalated. Exposure of $\text{H}(\text{C-T})\text{UP}$ to Br_2 vapor bleaches the purple

solids to a yellow color. A 12-h exposure was generally needed to fully eliminate the purple color. Accompanying this reaction, fig. 2 reveals that the C-T absorption band at 565 nm has largely disappeared; the resulting spectrum is characterized by the vibronic structure characteristic of UO_2^{2+} superimposed on the tail of a band whose intensity increases into the ultraviolet portion of the spectrum. The yellow color is consistent with the oxidation of the C-T complex to trivalent Ru centers [6], although the presence of the UO_2^{2+} absorption bands precludes determining whether the reaction produces the yellow, hexavalent binuclear complex, $[\text{Ru}(\text{NH}_3)_5]_2(\mu\text{-pyrazine})^{6+}$, and/or mononuclear complexes derived therefrom. Attempts to directly intercalate the hexavalent species into HUP were unsuccessful due to its instability in the neutral aqueous solution used for HUP intercalation reactions. Interestingly, we have seen partial regeneration of a purple color in the lattice over a period of days, presumably indicating formation of a divalent Ru species in the lattice [6].

The composition of $\text{H}(\text{C-T})\text{UP}$ after exposure to Br_2 was probed by infrared spectroscopy and X-ray analysis of a $\text{H}_{0.97}(\text{C-T})_{0.006}\text{UP}$ sample. Both the infrared spectrum and X-ray data for the oxidized solid were virtually identical to those of the starting material, indicating that no major structural change occurs to the host solid during the oxidation.

In general, we see more consequential variations in PL properties accompanying the oxidation of $\text{H}(\text{C-T})\text{UP}$ samples.

Although some samples show little change in PL intensity and decay times, most samples emit more brightly, presumably reflecting the diminution in self-absorption, and exhibit longer decay times; typical radiative efficiencies are 0.01 to 0.05, and decay times range from 50 to 200 μ sec. Some of the sample-to-sample variation may reflect differences in crystallinity and hydration. In general, however, PL efficiency and decay times in the oxidized samples are well below those of HUP, indicating that efficient quenching still obtains.

In summary, the C-T complex can be intercalated into HUP to yield a lamellar solid capable of undergoing redox chemistry discernible through substantial changes in electronic absorption and PL properties.

Acknowledgment

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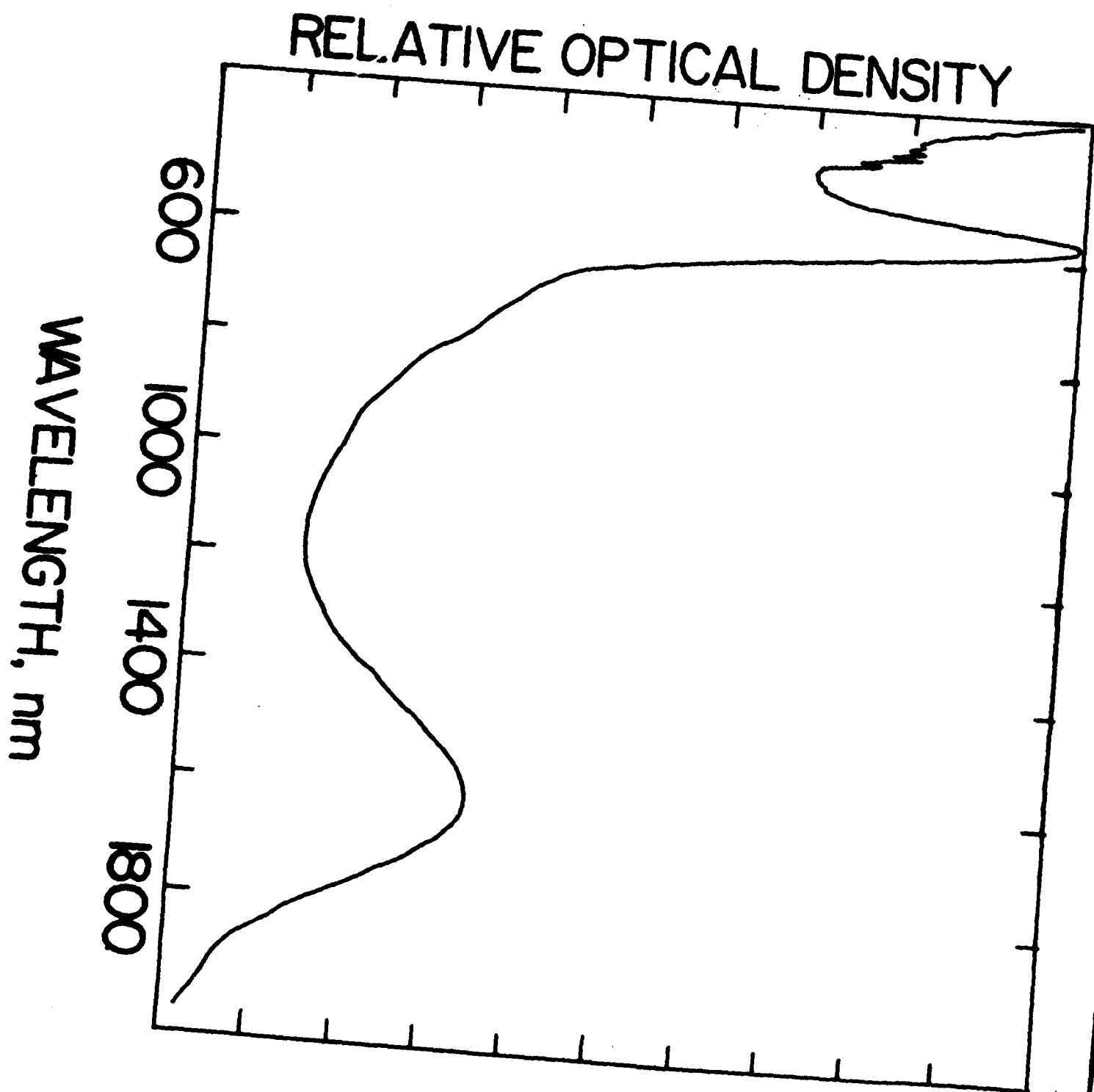
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Figure Captions

Figure 1. Absorption spectrum (295 K) of a sample of approximate composition $\text{H}_{0.95}(\text{C-T})_{0.01}\text{UP}$. The spectrum was obtained using a KBr pellet; a KBr pellet served as the reference.

Figure 2. Absorption spectrum (295 K) of a sample of initial approximate composition $\text{H}_{0.985}(\text{C-T})_{0.003}\text{UP}$, after a 12-h exposure to Br_2 vapor. The spectrum was obtained by spreading a silicone grease mull of the oxidized solid on filter paper; silicone grease on filter paper served as the reference.



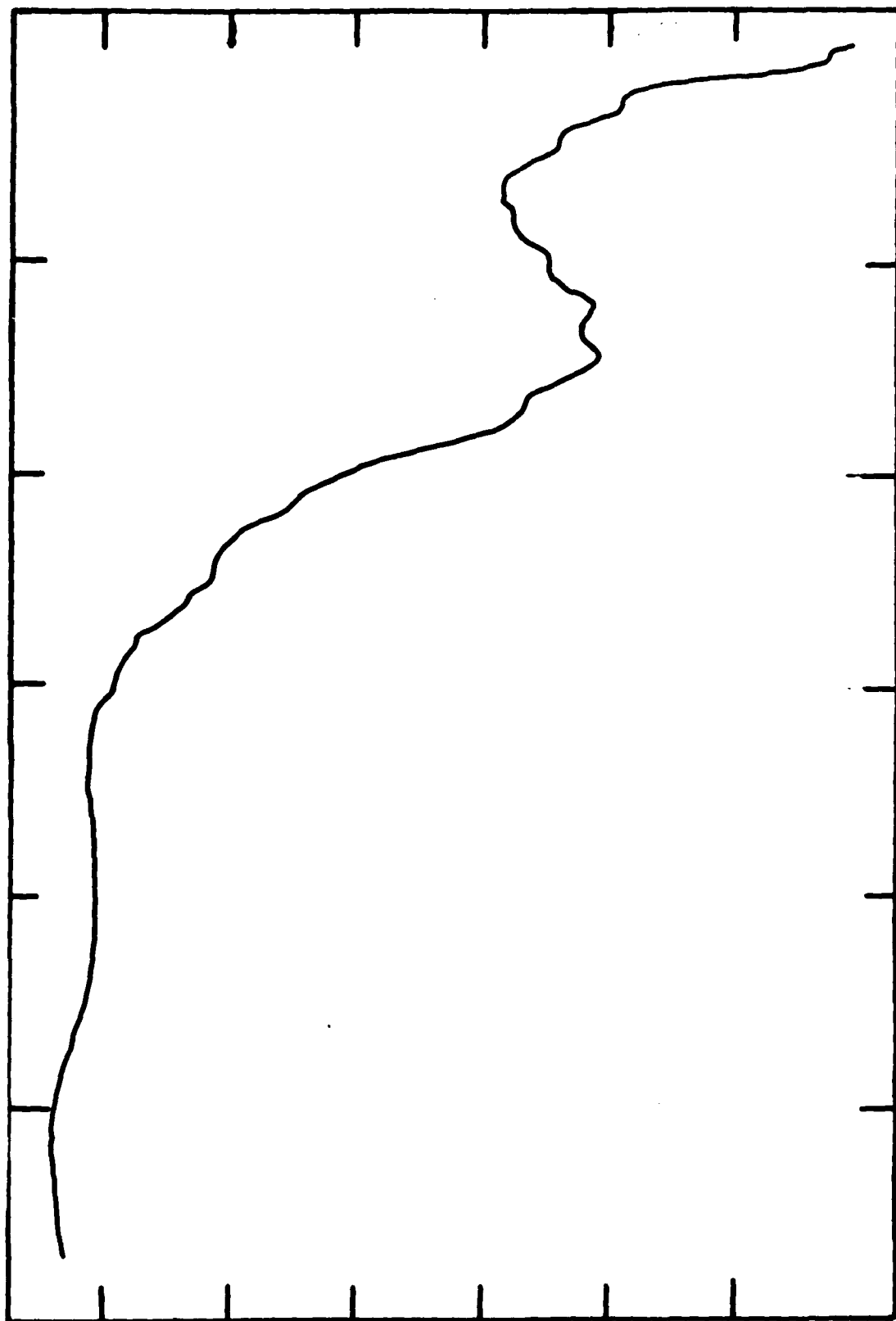
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